

A Lightweight NO₂ Instrument for Vertical Height Profiles

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ABSTRACT

A new lightweight NO₂ instrument that can be flown from a tethered balloon to give vertical NO₂ profiles is described. The detection principle is the chemiluminescent reaction between NO₂ and a solution of luminol. The instrument is integrated with a radiosonde to also give temperature, humidity, and pressure data. Tests show the instrument is linear from 2.8 to 75 ppbv but nonlinear below 2.8 ppbv. A calibration curve is determined. The sensitivity varies directly with pressure and it has a -3.5% per degree temperature dependence. Data from trial flights as part of the PACIFIC'93 field study show NO₂ data from the surface to 900 m.

1. Introduction

Nitrogen dioxide (NO₂) is a key compound in the troposphere. It is a criteria pollutant, but even more important is the role it plays in initiating tropospheric oxidant chemistry (Findlayson-Pitts and Pitts 1983). Since little radiation below 320 nm penetrates the stratosphere, NO₂ is the only gas that can be photodissociated to produce oxygen atoms in the troposphere. These atoms react almost exclusively with molecular oxygen to produce ozone, the primary atmospheric oxidant. Most of the other atmospheric oxidants (e.g., HO, HO₂, and H₂O₂) are generated from the reactions of the products of ozone photolysis. The radical oxidants, hydrocarbons, and the NO resulting from the NO₂ photolysis undergo reactions that oxidize both the hydrocarbon and the NO to regenerate the NO₂ that therefore acts as a catalyst for the production of ozone. This chemical system is nonlinear, making detailed understanding in all environments difficult.

To understand a real-world system, the sources of gases to the atmosphere, the way the meteorology dilutes and distributes them, and the chemistry all need to be considered. To do this, computer-based photo-

chemical models have been developed. These models contain source functions, meteorology, and chemical reaction mechanisms, and produce, as outputs, one-, two-, or three-dimensional concentration fields as a function of time. These models require quality measurements of trace gases to provide initial conditions and to test the validity of the output concentrations.

Given its key role in atmospheric chemistry, it is important that there are measurements of NO₂ with good time and location resolution. There have been several instruments developed for the measurement of tropospheric NO₂, but this measurement has proven particularly troublesome. The most widely used method relies on the conversion of NO₂ to NO, followed by the detection of the NO through its chemiluminescent reaction with ozone (Findlayson-Pitts and Pitts 1983). Unfortunately many converters, although they quantitatively convert NO₂ to NO, also convert other forms of nitrogen (such as nitric acid and organic nitrates) to NO providing a major interference in many situations. Recently, two more specific conversion methods have been developed. Kley and McFarland (1980) developed a UV photolytic converter that is usually coupled to a chemiluminescent NO monitor (e.g., Ridley et al. 1988). Sandholm et al. (1990) used a laser to photolyse the NO₂ and detected the resulting NO by laser-induced fluorescence. Tunable diode laser-based systems have provided a direct spectroscopic measurement of NO₂ (Schiff et al. 1983, 1990). An appealing direct measurement of NO₂ concentration can be obtained by instruments using NO₂'s chemiluminescent reaction with a solution containing luminol (5-amino-2,3-dihydro-1,4-phthalazine dione) (Maeda

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et al. 1980; Wendel et al. 1983; Schiff et al. 1986). These instruments are inherently smaller, lighter, and less complicated than the other instruments described above but have exhibited nonlinearity at low concentrations and are subject to interferences. The nonlinearity and the major interferences have been quantified (Drummond et al. 1989), and the technique is now widely used. The results of an intercomparison of a number of NO₂ instruments can be found in Fehsenfeld et al. (1990).

Many measurements of the tropospheric concentration of NO₂ have been reported. Most of these have been made at ground level, with only a limited number being made above the surface. In many cases the lack of vertical profile information limits the interpretation of observations and the testing of models. Aircraft measurements provide such information, but generally the number of vertical profiles is small. However, because of the speed and range of the aircraft, they provide very good spatial distributions. In contrast, balloon, motor glider, or kite platforms (Balsley et al. 1994; Dommen et al. 1995) can produce a larger number of profiles at a fixed location, at the expense of the spatial coverage. Aircraft can carry similar instrumentation to that used in ground stations; however, balloons and kites have very limited payloads so specific lightweight instruments are required.

This paper describes a lightweight sonde that has proven to be able to make real-time, vertical profile measurements of NO₂ from a balloon or kite platform. Such measurements are cheaper than those from aircraft; they can be made more frequently and can be more readily tailored to the local weather conditions. Furthermore, profiles can be made at the same location throughout the day to show the time evolution of the profile, a valuable test of photochemical models.

2. Instrumentation

The sonde operates by detecting the chemiluminescence produced when gas phase NO₂ reacts with a luminol solution in the presence of oxygen (Maeda et al. 1980). This oxidizes the luminol to produce a product that luminesces in the visible. The magnitude of this chemiluminescence is related to the NO₂ concentration. Several instruments using this principle have been built. Originally the air was exposed directly to the solution (Maeda et al. 1980). To overcome memory effects, later versions of the instrumentation passed the air over a thin film of the solution constrained to a paper or cloth wick (Wendel et al. 1983; Schiff et al. 1986). The sonde described here is of the latter type and is a smaller, lightweight version of the detector described in Schiff et al. (1986). It is integrated with a radiosonde that enables the package to measure temperature, humidity, and pressure in support of the NO₂ measurements and to telemeter the data to a computer-based

ground station. We have developed algorithms to correct the NO₂ signal for the temperature and pressure dependence and the inherent nonlinearity of the instrument. The package can therefore produce NO₂ temperature and humidity profiles as a function of height.

The sonde as presently configured consists of a reaction cell, systems to deliver the ambient air and the luminol solution to the cell, signal processing sections, and a full integration with the radiosonde. A block diagram of the instrument is shown in Fig. 1, with an electronic block diagram in Fig. 2. The sonde requires 5 W of 12–25-V dc power that can be supplied by 12 1.5-V AA-size alkaline batteries. Converters produce –800 V for the photomultiplier, +10, +5, and +6 V to run the electronics and the pumps. Twelve cells are sufficient for 3–4 h of operation, which corresponds to two tethered balloon flights from the surface to 1 km. The instrument is packaged into a 15 cm × 24 cm × 27 cm Styrofoam box and weighs approximately 3.25 kg, including batteries.

a. The reaction cell

The chemiluminescent reaction takes place when the NO₂ from the air sample dissolves into the luminol solution and initiates the oxidation. The solution contains luminol, sodium sulphite, and alcohol in a basic water solution of potassium hydroxide at pH 11.5 (Schiff et al. 1986). The sodium sulphite and alcohol have been shown to increase the chemiluminescence, that is, improve the instrument sensitivity, and the sulphite also reduces the interference due to other oxidants, notably ozone. The reaction cell is made of high-density polyethylene and holds a 5-cm² fabric wick down in which the luminol solution flows at 22 μL min⁻¹. Ambient air passes between the wick and an acrylic window that allows the photomultiplier to view the chemiluminescence.

b. Airflow system

The sensitivity of the instrument increases rapidly with airflow rate up to about 1 L min⁻¹, but very slowly above that. Consequently, the sample airflow is set at about 1.5 L min⁻¹ by the choice of voltage to the sample air pump (a rotary vane pump, Brey model 50110). This pump draws air through a half-meter-long section of 1/4" thin-wall TFE tubing and an ozone trap into the reaction cell. The cell constitutes the largest volume in the system (~50 mL) so the gas residence time in the system is approximately 2 s. In-flight testing of the instrument zero is achieved when the onboard computer activates a second pump to force approximately 2 L min⁻¹ of air through a scrubber, to remove NO₂, into the inlet system. Since this flow is greater than is drawn by the sample air pump, an excess of scrubbed air flows out of the sonde inlet.

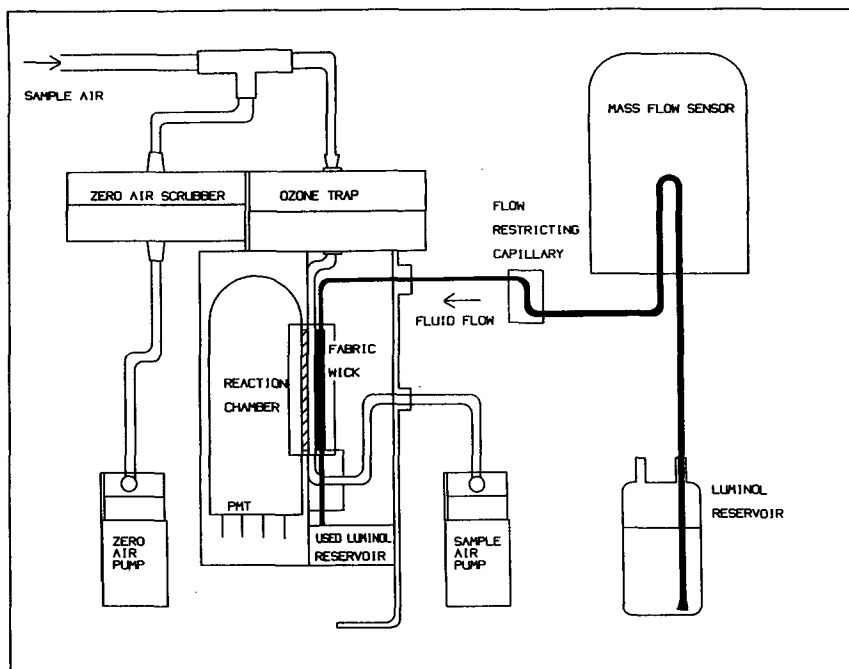


FIG. 1. Mechanical block diagram for the NO₂ sonde.

Drummond et al. (1989) showed the luminol detector to respond to ozone with a sensitivity less than 1% that of NO₂. However, even at that level, the interference could be significant in a number of environments. Therefore to remove this interference, an ozone trap (Unisearch Associates Inc., O₃ scrubber) is inserted immediately before the reaction cell. Tests have shown this scrubber is capable of removing ozone at ambient levels without affecting the NO₂ concentration (Drummond et al. 1989).

c. Liquid flow system

The luminol solution is drawn from a glass reservoir, through a flowmeter, and a flow restricting capillary, to the wick in the reaction vessel by the slight negative pressure produced by the sample air pump. Liquid is transferred from the tubing to the wick by contact. The response of the sonde is highly dependent on the liquid flow rate at low NO₂ mixing ratios (<2 ppbv). Consequently, the liquid flow is controlled to within 20%

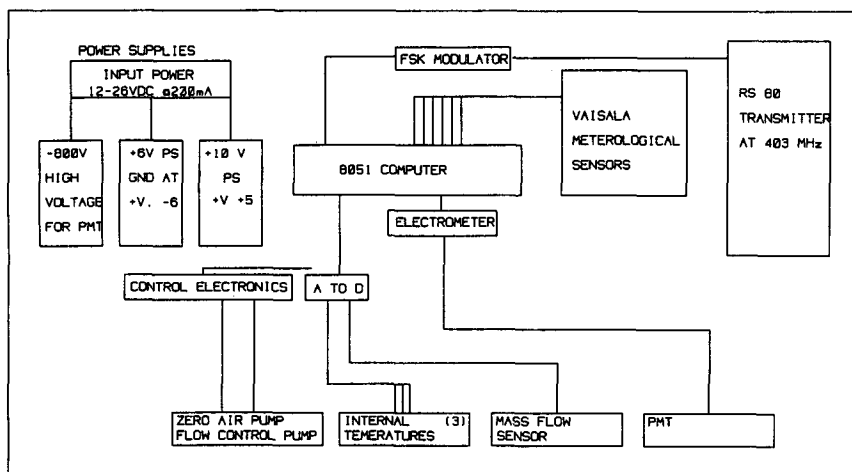


FIG. 2. Electronic block diagram for the NO₂ sonde.

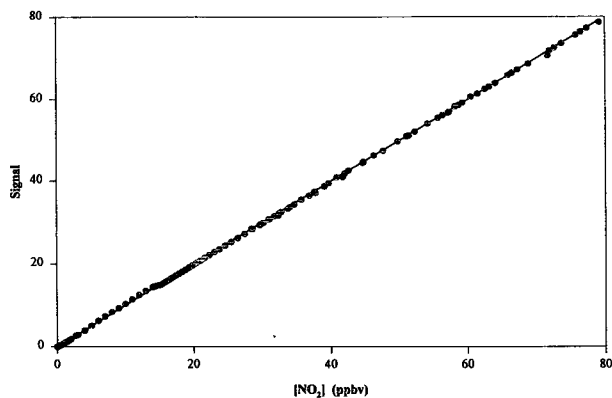


FIG. 3. Calibration curve for the NO_2 sonde over the full range of calibration. The sonde was calibrated at 10.6 ppbv, and the signal quoted is the signal divided by the sensitivity. Points are the data; the line is linear part of the calibration equation.

of the desired $22 \mu\text{L min}^{-1}$. The liquid flow rate is measured by a flowmeter (Unisearch Associates) that consists of a heated stainless steel capillary and two temperature sensors located at equal distances from the heater. The fluid carries heat from the heater to the downstream sensor and the difference between the two sensors is proportional to the liquid flow rate. Flow control is achieved by a servo system that varies the speed of the airflow pump. The variation in pump speed required to maintain the liquid flow stability does not change the airflow enough to affect the instrument's sensitivity.

d. Integration with the radiosonde, signal processing, and data transmission

The NO_2 sonde and a radiosonde (Vaisala RS80) are integrated into a single package. The meteorological sensors were moved from the radiosonde into the NO_2 sonde so that control of all the data is performed by the onboard computer.

The radiation from the chemiluminescent reaction is detected by a Hamamatsu R906 photomultiplier tube (PMT) that has a maximum sensitivity in the region 410–450 nm, similar to the peak wavelength region for the chemiluminescence. The current from the PMT is measured by an electrometer whose output is then converted to a frequency for counting.

The onboard computer reads all signals and generates a data frame every 5 s. This includes an identification number, a 5-s count of the PMT frequency output, instrument temperature, liquid flow rate, battery voltage, and the meteorological data. These data are converted to a serial data stream at 1200 baud and sent as frequency shift keying (FSK) ASCII characters to the radiosonde's frequency modulated transmitter, which is now powered from the NO_2 sonde.

The telemetered signal is received by an ICOM FM receiver. The resulting audio output is demodulated to recover the RS232 characters that are sent to a personal computer to be preprocessed and recorded. Postflight data analysis includes correction of the NO_2 data for instrument nonlinearities and pressure and temperature corrections (see below).

3. Instrument calibration and testing

The details of the chemiluminescent reaction between NO_2 and luminol are not completely known, and instruments using this reaction are known to have a nonlinear response to NO_2 at low concentrations (Drummond et al. 1989). Therefore, each instrument and instrument design requires independent calibration. Laboratory calibrations and linearity tests were performed on the sonde, over the range of 0.2–75 ppbv of NO_2 . Two NO_2 permeation devices were necessary to accurately produce concentrations over such a wide concentration range. One tube was used to produce concentrations from 0.2 to 15 ppbv, while the other from 12 to 75 ppbv. The tube with the larger permeation rate was calibrated by weight loss. The other was calibrated against a standard mixture of NO_2 using a luminol-based NO_2 detector (Unisearch Associates LMA 3). A ppbv mixture of NO_2 , at approximately the same concentration as generated from the permeation tube, was produced by diluting a 6-ppmv standard of NO in N_2 (Scott Speciality Gases, Certified Standard) with synthetic air and passing the mixture through a chromium trioxide converter that quantitatively converts the NO to NO_2 . Comparison between the two permeation tubes where they overlapped concentrations (12–15 ppbv) showed agreement within 10%. Thus, the calibrations of the two tubes are consistent. The sonde was zeroed, calibrated at 10.6 ppbv, and

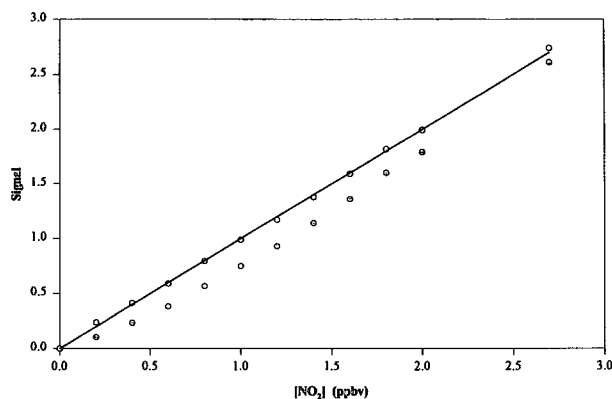


FIG. 4. As for Fig. 3 but only for concentrations up to 3 ppbv. Solid points are the signal; the open points are the calculated concentrations from the equation for $S \leq 2.8$ ppbv (see text). The 1:1 line is also shown.

presented with the range of concentrations. Figure 3 shows the measured NO_2 signal, counts per sensitivity, as a function of the generated NO_2 concentration with the nonlinear region being expanded in Fig. 4. The slight difference between the two calibration sources shows as a discontinuity, in Fig. 3, at around 15 ppbv. The data are best fit by the following two equations:

$$[\text{NO}_2]_a = \begin{cases} 0.74S + 0.50S^{1/2}, & S \leq 2.8 \\ S + 0.13, & S > 2.8, \end{cases}$$

where S is the signal from the sonde and $[\text{NO}_2]_a$ is the ambient concentration. The lower equation is plotted in Fig. 3, and for Fig. 4 the $[\text{NO}_2]_a$ values calculated by the upper equation are plotted as well as the 1:1 line. These equations overlap smoothly around 2.8 ppbv so there are no discontinuities in the data workup. It should be noted that this equation is different than that derived for the ground-based monitor (Drummond et al. 1989), particularly with regard to the concentration below which nonlinearity of response occurs. As the same formulation of luminol solution was used for both calibrations, this suggests that the geometry of the reaction chamber and the liquid flow rate may be factors in determining the instrument response.

The sensitivity of the sonde is dependent on both pressure and cell temperature. Figure 5 shows that, for a constant mixing ratio (10.6 ppbv) at constant temperature, the sensitivity scales proportionally with pressure, over a range of pressures much larger than expected in tethered balloon applications. This indicates that the sonde measures the concentration of NO_2 rather than its mixing ratio. We generally report measurements as mixing ratios; therefore, the raw data are corrected by multiplying by the ratio of the reference to ambient pressure. The temperature dependence of the sonde is repeatable and shown in Fig. 6. Over the range of temperatures expected to be encountered, the sen-

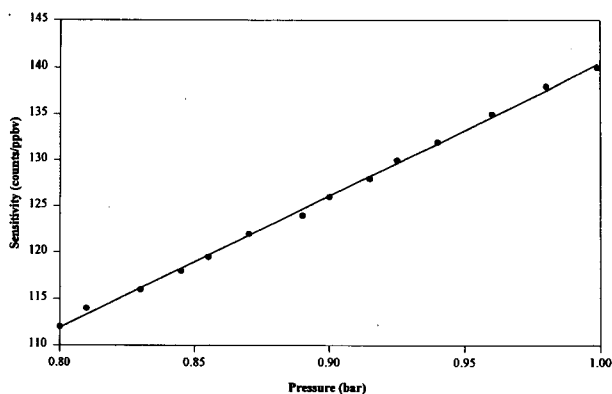


FIG. 5. Pressure dependence of the NO_2 sonde. Measurements are at room temperature for 10.6-ppbv NO_2 .

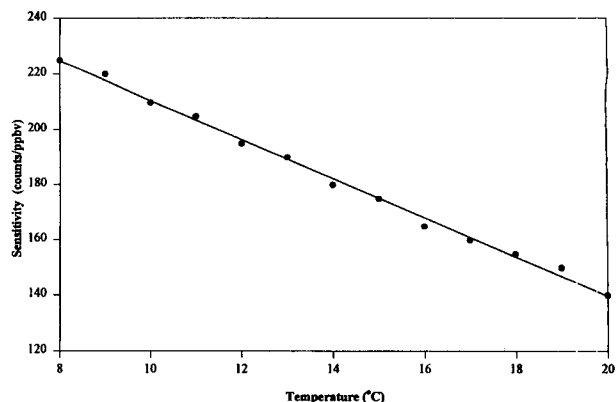


FIG. 6. Temperature dependence of the NO_2 sonde. Measurements are for 10.6-ppbv NO_2 . Points are the data obtained; the line is the linear least squares fit to the data.

sitivity decreases by 7.1 counts per ppbv per degree, or about 3.5%. In reality this is a very small correction as it pertains to the temperature of the reaction cell that, because of the insulation and the heat generated by the instrument, experiences much smaller temperature variations than exist in the ambient environment.

Tests showed that the sonde had no response to ozone when the ozone scrubber was in place. Drummond et al. (1989) showed the luminol detector to respond to peroxyacetyl nitrate (PAN) with a sensitivity approximately 25% that of NO_2 . Since we are using the same solution as Drummond et al., we have taken this to be the level of PAN interference for the sonde.

4. Field tests

The sonde was deployed on an A.I.R. tethered balloon on 4 days as part of the PACIFIC'93 field study in Vancouver, British Columbia. For the early part of the study the sonde was flown along with an meteorological sonde and an ozonesonde (A.I.R.) on a 7-m³ balloon. This balloon was lost, with the sonde free-falling about 300 m, so a smaller balloon had to be used for the last 2 days. This balloon did not have sufficient lift to carry all the sondes, so the NO_2 sonde was flown separately from the meteorological and ozone sondes. The NO_2 sonde produced data on 15 of the 19 flights that gave 29 vertical profiles. The major problem encountered was interference in the telemetry that resulted in a loss of data. Generally this was only about 10% of the total but in the worst case was 50%, since this time the FSK demodulator has been rebuilt to improve the noise rejection.

The instrument was calibrated using a 10.6-ppbv NO_2 standard from a permeation tube before and after each flight. No sensitivity changes were found. During each flight, zero air was added for 1 min each 15 to test for zero drift, but no drift was found. The liquid flow

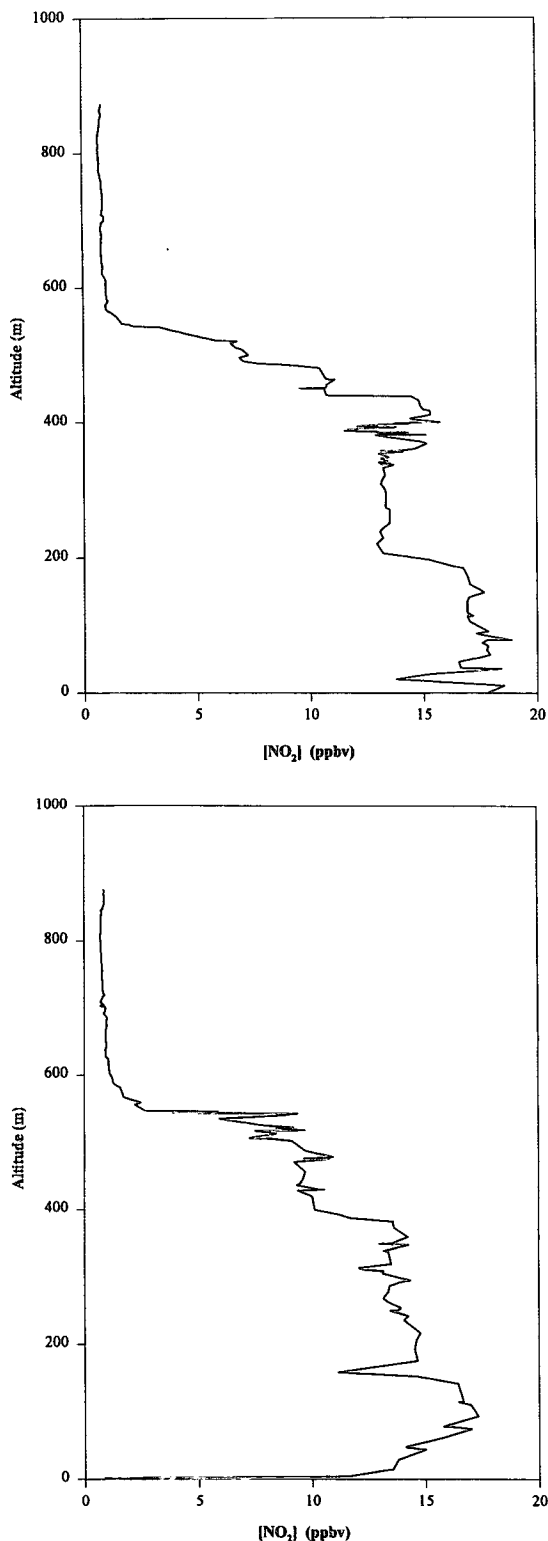


FIG. 7. Measured NO_2 concentration as a function of height for a flight on 1 August 1993 in the Lower Fraser Valley, British Columbia. Upper plot: data on ascent (0942–1012 PST). Lower plot: data on descent (1013–1043 PST).

remained within 20% of the optimal $22 \mu\text{L min}^{-1}$ over 95% of the time, and the reaction vessel temperature varied by only 2°C .

Figure 7 presents data obtained from the NO_2 sonde during a single flight on 1 August 1993. The NO_2 concentration is plotted against height, as determined from the pressure and temperature, for both the balloon ascent and the descent. On this day the PAN concentration at the surface was less than 0.6 ppbv (J. Bottenheim 1994, personal communication), so the PAN interference was less than 0.15-ppbv NO_2 equivalents. Since the measured boundary layer NO_2 concentration was greater than 5 ppbv, the PAN interference is negligible. The data clearly show the high NO_2 concentration in the boundary layer compared to the free troposphere, as expected in an urban environment. The coincidence in the boundary layer heights as obtained from the NO_2 measurements with the balloon moving in the two directions shows that the time response of the instrument is fast compared to the balloon's vertical motion. There is some reproducibility in the structure of the NO_2 profile between the flights that shows that the observed variation in concentration with height is likely real and not a manifestation of noise in the sonde. The data from this measurement campaign have been combined with the ozone measurements and will be reported elsewhere.

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